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FORTULAN, Raphael <<http://orcid.org/0000-0002-1234-5212>> and YAMINI, Sima Aminorroaya <<http://orcid.org/0000-0002-2312-8272>>

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Recent Progress in Multiphase Thermoelectric Materials

Raphael Fortulan ¹ and Sima Aminorroaya Yamini ^{1,2,*}

¹ Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, UK; b9044884@my.shu.ac.uk

² Department of Engineering and Mathematics, Sheffield Hallam University, Sheffield S1 1WB, UK

* Correspondence: s.aminorroaya@shu.ac.uk

Abstract: Thermoelectric materials, which directly convert thermal energy to electricity and vice versa, are considered a viable source of renewable energy. However, the enhancement of conversion efficiency in these materials is very challenging. Recently, multiphase thermoelectric materials have presented themselves as the most promising materials to achieve higher thermoelectric efficiencies than single-phase compounds. These materials provide higher degrees of freedom to design new compounds and adopt new approaches to enhance the electronic transport properties of thermoelectric materials. Here, we have summarised the current developments in multiphase thermoelectric materials, exploiting the beneficial effects of secondary phases, and reviewed the principal mechanisms explaining the enhanced conversion efficiency in these materials. This includes energy filtering, modulation doping, phonon scattering, and magnetic effects. This work assists researchers to design new high-performance thermoelectric materials by providing common concepts.

Keywords: thermoelectric materials; multiphase; composite; energy filtering; magnetic effect; phonon scattering

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1. Introduction

Thermoelectric (TE) materials have been attracting a great deal of interest because of their applications in energy recovery from industrial waste heat and high-efficiency cooling of next-generation integrated circuits [1]. The efficiency of TE materials is characterised by a dimensionless figure of merit $zT = S^2\sigma T/(\kappa_e + \kappa_l)$, where T , S , σ , κ_e and κ_l are the absolute temperature, Seebeck coefficient, electrical conductivity, and electronic and lattice components of the total thermal conductivity (κ_t), respectively. Most thermoelectric materials used in commercial applications have a zT of around 1 [2], which corresponds to an efficiency of roughly 10% in the medium temperature range [3]. To increase zT , one would need to increase S and σ and decrease κ_t . These parameters are interrelated though; the electronic thermal conductivity increases with the increase of electrical conductivity, and S and σ are inversely proportional [4]. Therefore, optimising these parameters is very challenging and the key to achieving higher efficiency.

One of the most successful approaches to improve the figure of merit is reducing the lattice thermal conductivity, and over the years, various phonon engineering approaches have been used to enhance phonon scattering and decrease κ_l by taking advantage of nanoprecipitates [5–7], alloying elements [8–10], nanostructured grain boundaries [11–14], ionised impurities [15,16], and superlattices [17].

A series of band structure engineering approaches have also been employed to improve the electronic properties [18–20]. Strategies such as quantum confinement [21,22], modulation doping [23–25], introducing resonance energy to the electronic density of states [26,27], and energy filtering [28] are being actively pursued. These strategies are adopted to modify the band structure and transport properties of the

thermoelectric materials by either tuning the electrical conductivity and the Seebeck coefficient independently or by increasing them simultaneously. In practice, the best results were achieved with a significant increase in one of these parameters and a slight decrease in the other, resulting in an increase in the power factor ($S^2\sigma$) and zT .

The development of highly efficient thermoelectric materials encountered a bottleneck when the exploration of single-phase alloys was exhausted. Therefore, investigating multiphase compounds is the most viable strategy to enhance the thermoelectric performance of bulk materials, where higher degrees of freedom are available to design new materials and tune their electronic transport properties [29–31]. Figure 1 presents the number of yearly publications on thermoelectric materials, indexed by the Scopus database, compared with the numbers of papers published on multiphase/composite thermoelectric materials, indicating an increasing interest of the research community on this topic over the last five years.

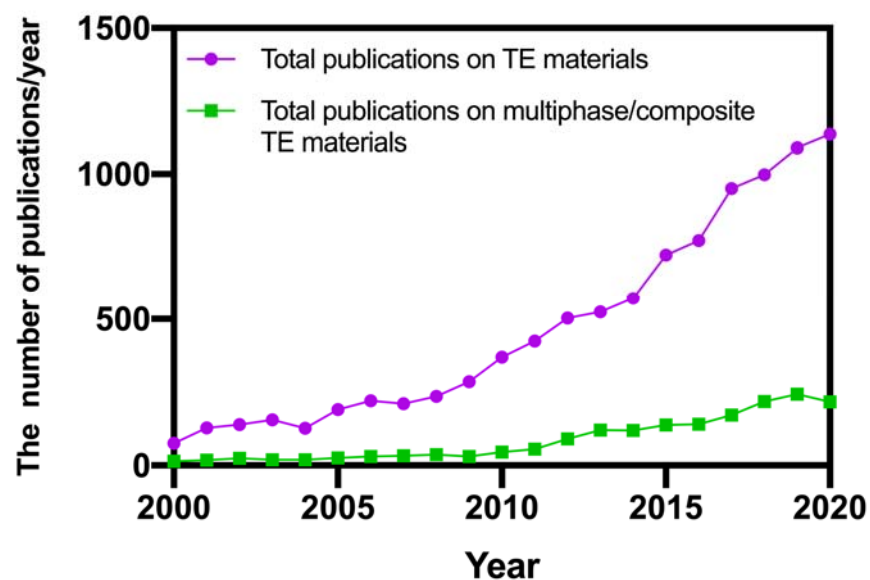


Figure 1. Yearly number of publications on thermoelectric materials, compared with publications on multiphase/composite thermoelectric materials.

The combination of several phases can improve the electrical conductivity, Seebeck coefficient, and thermal conductivity [32]. Here, we summarise the main strategies discovered to date to increase the thermoelectric efficiency in multiphase materials. This includes: (1) energy filtering, creating potential barriers in the electronic band structure of the main phase through interfaces with the secondary phases. This results in an increase in the overall Seebeck coefficient [33–35]; (2) modulation doping, where the heterojunctions between secondary phases with larger bandgaps and higher carrier concentrations than the matrix are used to greatly increase the electrical conductivity of the multiphase compounds [36–38]; (3) phonon scattering by interfaces, grain boundaries, and defects to reduce the lattice thermal conductivity [39–42]; and (4) magnetic effects, which utilises the magnon-drag mechanism in magnetic materials [43–45], semiconductors doped with magnetic elements [46–48], or semiconductors containing secondary magnetic phases [49,50] to improve the thermoelectric efficiency [51,52].

2. Energy Filtering

The concept of energy filtering in thermoelectric materials was first introduced and studied in the latter half of the last century [53]. The research on this field has been renewed and developed since the 1990s. In general, the Seebeck coefficient increases with an increase of the barrier height [54,55] while the electrical conductivity decreases [56–58].

In the presence of multiple potential barriers, the bipolar effect can be suppressed, decreasing the flow of minority charge carriers and reducing the decrease in the electrical conductivity [59–62].

Conventionally, the energy filtering effect could be understood by solving the Boltzmann transport equation (BTE) using the relaxation time approximation [63,64]. The BTE equation expresses all thermoelectric transport coefficients as a function of the energy-dependent relaxation times of the charge carriers $\tau(E)$ and the Fermi level E_F . The energy filtering effect can be readily verified considering the Seebeck coefficient expression [65]:

$$S = -\frac{1}{qT} \frac{\int (E - E_F) \sigma'(E) dE}{\int \sigma'(E) dE} \quad (1)$$

where T is the absolute temperature, E is the charge carrier energy, E_F is the Fermi level, and σ' is the differential conductivity. The Seebeck coefficient, as shown in Equation (1), is the energy average weighted by the electrical conductivity:

$$S = -\frac{1}{qT} \langle E - E_F \rangle_{\sigma'} \quad (2)$$

implying that an asymmetry between the density of states and the Fermi level can create higher Seebeck coefficients.

The implementation of energy barriers in thermoelectric materials is made in the form of either nanoparticles or grain boundary interfaces embedded in the bulk host matrix [66]. At these interfaces, the carriers with higher energy will pass the interface preferentially, while the carriers with lower energy are filtered out. A high density of the interfaces ensures the positive carrier filtering effect [67]. The band bending between the two materials creates an energy barrier that reflects the charge carrier [68,69]. Figure 2 illustrates the energy filtering effect: given the partial reflection of the lower energy electron waves, the high energy electrons mostly contribute to the Seebeck coefficient.

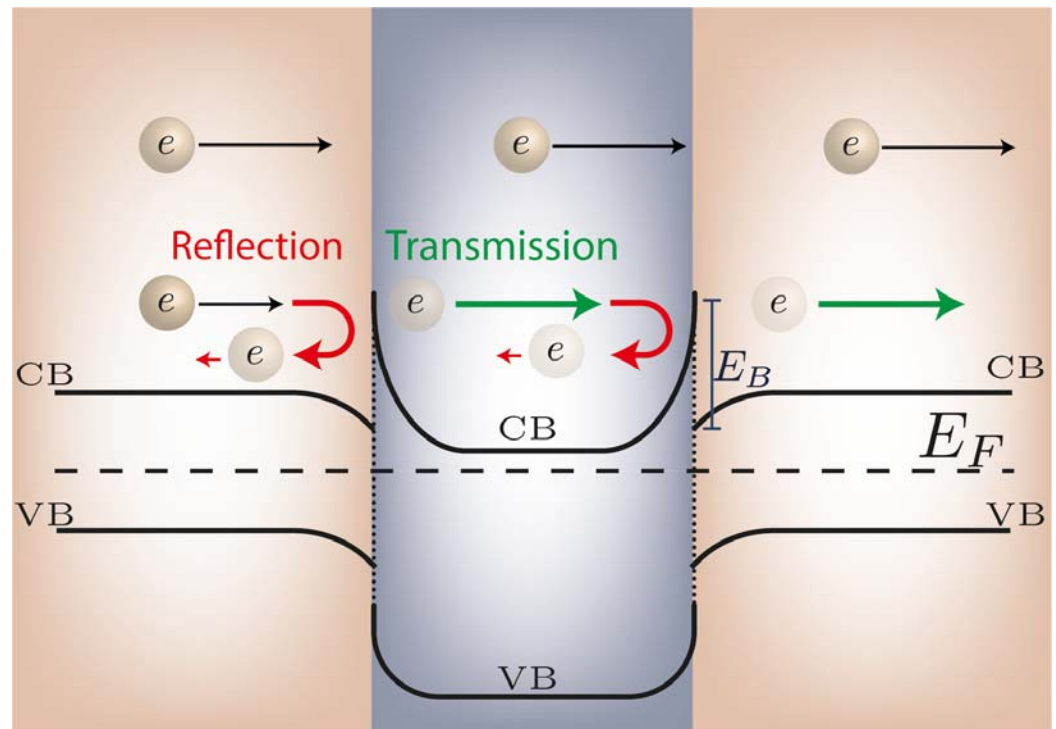


Figure 2. Energy filtering effect, showing that lower energy electrons are scattered by a potential barrier.

Multiphase materials present themselves as viable candidates to take advantage of energy filtering. Given the possibilities of tuning the electronic band structure of each phase, the band bending can noticeably enhance the energy filtering effect [70–77]. In the following sections, the energy filtering effect will be discussed in multiphase materials. A Schottky or ohmic barrier will appear at the interface with a metallic secondary phase, while a heterojunction barrier will present at the interface of thermoelectric material with a semiconducting secondary phase.

2.1. Energy Filtering by Metal Secondary Phases

For metallic phases, the barrier height will be proportional to the work function of both the semiconductor and the metal and the electron affinity of the semiconductor. The work function, Φ , is defined as the minimum energy required to remove an electron from the surface of a material, and its value is equal to the energy difference between the vacuum and the Fermi level [78]. The electron affinity, χ , is the energy difference between the vacuum and the bottom of the conduction band. At the metal–semiconductor junction, the Schottky–Mott rule [79] defines the barrier height, E_B , to be the difference between the metals' work function, Φ_M , and the semiconductor electron affinity, χ_S :

$$E_B = \Phi_M - \chi_S \quad (3)$$

Small differences cause few restrictions on the movement of the electrons, and this barrier is known as ohmic. Both the work function and electron affinity depend on the surface impurity and the crystallographic orientation.

Theoretically, the presence of metals can strongly affect the carrier relaxation time and consequently affects both the electrical conductivity and the Seebeck coefficient [54,80,81]. The inclusion of metallic nanoparticles was shown to enhance the Seebeck coefficient mathematically [66]. The interface of *n*-type PbTe with metallic Pb nanoparticles, with a low work function, effectively scattered the electrons and increased both the Seebeck coefficient and electrical resistivity. This mechanism is illustrated schematically in Figure 3, where spherical metallic nanoparticles are randomly distributed in a host semiconductor.

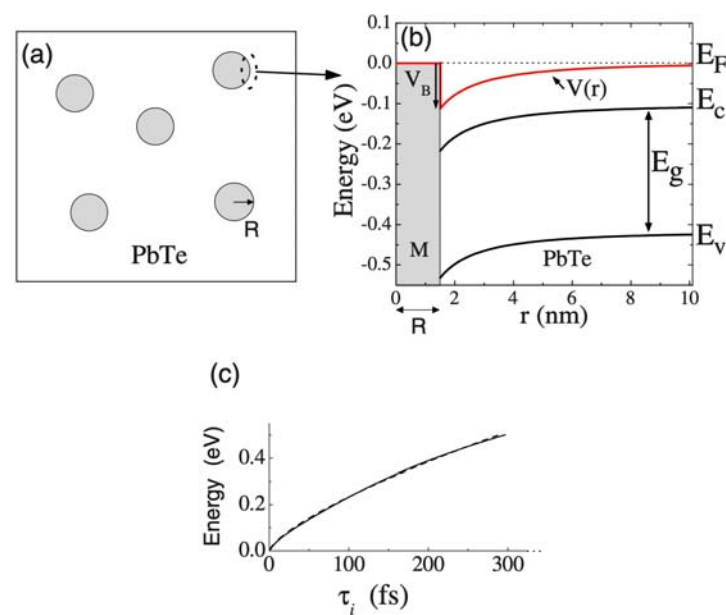


Figure 3. (a) Schematic of randomly distributed metallic Pb secondary phase in a PbTe matrix (b) Calculated potential $V(r)$ and energy diagram for PbTe at 300 K, carrier concentration of $2.5 \times 10^{19} \text{ cm}^{-3}$, barrier height of 0.11 eV, and radius of 1.5 nm, where E_F is the Fermi level, E_C is the energy at the bottom of the conduction band, E_g is the band gap, and E_V is the energy at the top of the valence band (c) Carriers' relaxation time as a function of their energy. Reprinted from [66].

Experimental results have proved this concept [82–84]: for instance, Pb precipitates in the matrix of *n*-type PbTe, intrinsically doped with excess Pb, increased the Seebeck coefficient and the average resistivity from $-98 \mu\text{V/K}$ and $1.2 \text{ m}\Omega \text{ cm}$ for $\text{Pb}_{1.03}\text{Te}$ to $-130 \mu\text{V/K}$, and $3.2 \text{ m}\Omega \text{ cm}$ for $\text{Pb}_{1.06}\text{Te}$ at 300 K, respectively [82]. The addition of metallic Sn and Cr to Cu_2O doubled the Seebeck coefficient from $700 \mu\text{V/K}$ to $1400 \mu\text{V/K}$ [84]. Platinum nanocrystals created energy barriers in *p*-type Sb_2Te_3 thin films [83] and caused a large reduction in carrier mobility in about 2.5 orders of magnitude due to the additional scattering of charge carriers compared to Sb_2Te_3 films without Pt nanocrystals. The carrier concentration increased, possibly due to the overlapping of energy bands [66]. The band overlapping increases the distance between the Fermi energy level and the valence band maxima, thereby increasing the total concentration of holes in the semiconductor matrix.

Silver nanoparticles enhanced the Seebeck coefficient of CdO-Ag composites [85]—a potential barrier of $E_B = 0.1 \text{ eV}$ between the work function of Ag and the electron affinity of CdO increased the resistivity from $1.5 \text{ m}\Omega \text{ cm}$ to $1.7 \text{ m}\Omega \text{ cm}$ for a sample with 0.03% of Ag and increased the Seebeck coefficient from $-120 \mu\text{V/K}$ for the pristine sample to $-129 \mu\text{V/K}$ for the sample with 0.03% of Ag at 800 K.

2.2. Energy Filtering by Semiconducting Secondary Phases

For a semiconductor secondary phase, the difference between the bandgaps and Fermi levels of the two phases gives rise to a potential barrier at their junction [86]. The barrier height will be proportional to the difference between the electron affinity of the two semiconductors (χ_1, χ_2). Anderson's rule [78] allows a simple estimate of the barrier height at the conduction, E_{BC} , and valence, E_{BV} , bands:

$$E_{BC} = \chi_2 - \chi_1 \quad (4)$$

$$E_{BV} = (E_{g1} - E_{g2}) - E_{BC} \quad (5)$$

and it has been employed as a rough estimation to design multiphase materials. The actual curvature of the band bending can be found using Poisson's equation for the electric potential [87]:

$$-\nabla^2 V = \frac{\rho}{\varepsilon} = \frac{q(h - n + D)}{\varepsilon} \quad (6)$$

where ε is the permittivity of the material, h and n are the holes and electrons densities, respectively, and D is the concentration of ionised impurities (extrinsic dopant). The relation of the barrier height and conductivity is suggested as [88]:

$$\sigma \propto T^{-\frac{1}{2}} e^{-\frac{E_B}{k_B T}} \quad (7)$$

It should be noted that this equation was developed for homojunctions [89,90]. However, experimental data for heterojunctions fit this equation surprisingly well [91]. Experimental results show that energy filtering caused by dissimilar semiconducting phases can improve the power factor [92–95]. Silicon oxide particles in the $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ bulk alloy increased the Seebeck coefficient from $182 \mu\text{V/K}$ for the pristine sample to $218 \mu\text{V/K}$ for the sample with 1.1% volume of SiO_2 at room temperature [92]. Yttrium oxide (Y_2O_3) particles embedded in a $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ matrix increased the Seebeck coefficient significantly [96], deviated considerably from the ideal Pisarenko relation. The Seebeck coefficient is inversely proportional to the carrier concentration, n , by a rate of $n^{-2/3}$ for degenerate semiconductors, according to the Pisarenko relation [97]. The deviation from this ideal relationship has been used as an indication of changes in the electronic band structure of the material [98].

Randomly dispersed titanium dioxide nanoparticles (ranging from 10 to 25 nm) in a $\text{Ba}_{0.22}\text{Co}_4\text{Sb}_{12}$ matrix increased the Seebeck coefficient [99]. Although the bandgap for $\text{Ba}_{0.22}\text{Co}_4\text{Sb}_{12}$ was unknown, given the large bandgap of TiO_2 (3.2 eV [100]), some influence of the energy filtering was assumed. At 300 K, the electrical conductivity decreased from

2.9×10^5 S/K to 2.8×10^5 S/K, and the Seebeck coefficient increased from -105 μ V/K for the pristine sample to -110 μ V/K for the sample with 0.8% volume of TiO_2 . The TiO_2 particles in Bi_2Se_3 based materials increased the overall power factor of the composite from 0.75×10^{-3} W/m K to 1.07×10^{-3} W/m K for the sample with 10 wt.% of titanium dioxide [101]. The charge carrier concentration varied greatly with the concentration of TiO_2 , possibly due to the formation of Ti^{2+} ions during hot pressing under the vacuum.

Interestingly, a double-filtering effect has been reported for a deposited TiO_2 on $\text{TiC}_{1-x}\text{O}_x/\text{TiO}_y$ ($x < 1$, $1 < y < 2$) heterostructures (Figure 4) [102]. $\text{TiC}_{1-x}\text{O}_x$, with a narrow bandgap and high electrical conductivity, in combination with TiO_y and TiO_2 nanoparticles, with wide bandgaps, produced an effective barrier height for energy filtering. The Seebeck coefficient and resistivity of the samples increased where a larger amount of TiO_2 was deposited. The maximum value obtained for the Seebeck coefficient at 973 K was -156 μ V/K, with an electrical conductivity of $\sim 4 \times 10^4$ S/m.

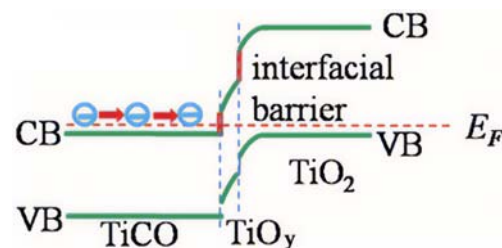


Figure 4. Band diagrams of the $\text{TiC}_{1-x}\text{O}_x/\text{TiO}_y\text{-TiO}_2$ heterostructured interface, where CB is the conduction band, VB is the valence band, and E_F is the Fermi level. Reprinted from [102].

Silicon-based materials, although not common in thermoelectricity, have also been shown to benefit from energy filtering [103–110]. For instance, heavily doped Si with B with nanoparticles of Si has shown an increased Seebeck coefficient and electrical conductivity in a particular range of dopant concentrations [111]. The increased Fermi level for the bulk material explains the increase of the electrical conductivity, and the energy filtering effect justifies the increased Seebeck coefficient.

A half-Heusler compound of $(\text{Hf}_{0.6}\text{Zr}_{0.4})\text{NiSn}_{0.99}\text{Sb}_{0.01}$, with added nanoparticles of tungsten (W), showed a maximum zT of 1.4 at 873 K and average zT of 0.9 in the temperature range of 300–973 K for the alloy with 5 wt.% tungsten nanoparticles [112].

Table 1 summarises the compositions and fabrication methods of recent studies that reported energy filtering effects in multiphase thermoelectric materials.

Table 1. Compositions, fabrication methods, and corresponding references of multiphase materials that benefited from the energy-filtering effect.

Composition	Fabrication Technique	Ref.
$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te} + (0, 1.0, 2.0, 4.0, \text{ and } 6.0 \text{ wt.}\%)$ nanoparticles of Sb_2O_3	Casting ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}$) + ball milling of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}$ and commercial powder of Sb_2O_3 + sintering	[113]
$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder + ~ 2 nm layer of film of ZnO	Solution-based synthesis of Bi-Te-Se powder + atomic layer deposition of ZnO + hot pressing	[114]
$\text{Bi}_{1-x}\text{Sb}_x$ ($x = 0, 0.10, 0.12, 0.13, 0.14, 0.2$) + 3 wt.% carbon nanotubes	Ball milling + cold pressing + annealing	[115]
$\text{Bi}_{0.46}\text{Sb}_{1.54}\text{Te}_3 + (0, 0.1, 0.2, \text{ and } 0.3 \text{ wt.}\%)$ SiC	Ball milling + sintering	[70]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3 + (0.1\%, 0.2\%, \text{ and } 0.3 \text{ wt.}\%)$ CuInTe ₂	Casting each phase separately + ball milling + sintering	[116]
$\text{Lu}_{0.1}\text{Bi}_{1.9}\text{Te}_3 + (0, 0.0, 0.05, 1) \text{ wt.}\%$ carbon nanotubes	Hydrothermal synthesis + grinding + hot pressing	[117]
$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + (0, 0.1, 0.2, 0.3, 0.4 \text{ wt.}\%)$ BaTiO ₃	Hydrothermally synthesised BaTiO ₃ + Commercial ingots of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ were grinded and sintered	[74]
$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + \text{SrTiO}_3$	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ films were grown on SrTiO_3 substrates by co-sputtering	[118]
$\text{Bi}_2\text{Te}_3 + \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thin films	Radio-frequency magnetron sputtering of $\text{Bi}_2\text{Te}_3/\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ layers on a $\text{SiO}_2/\text{Si}(001)$ substrate	[119]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3 + (0, 0.2, 0.4, \text{ and } 0.6 \text{ vol.}\%)$ CuGaTe ₂	Vacuum melting + hot pressing	[120]

$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + 2 \text{ wt.}\% (\text{Gd}_2\text{O}_3, \text{Gd}_{1.98}\text{Bi}_{0.02}\text{O}_3)$	Powders for each phase were prepared by induction melting then mixed by spray pyrolysis + sintering	[121]
$\text{Bi}_2\text{Te}_3 + (1, 2, \text{ and } 5 \text{ wt.}\%) \text{ SnS}$	Commercial powders were mixed, cold pressed, and annealed	[122]
$\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3 + (0, 0.25, 0.50, \text{ and } 0.75 \text{ wt.}\%) \text{ TiC}$	Ball milling + sintering	[123]
$\text{Bi}_2\text{Te}_3 + \sim 4 \text{ wt.}\% \text{ of } \text{Cu}_{1.5}\text{Te}$	Solution-based synthesis (each phase separately) + hot pressing	[124]
Coated grains of SnTe with CuInTe_2	CuInTe_2 was formed by cation exchange of Sn by Cu and In on the surface of ball-milled SnTe powder	[125]
$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3\text{-Cu}_{0.07} + (0, 0.5, \text{ and } 1.0 \text{ wt.}\%) \text{ HfO}_2$	Water atomisation + ball milling + sintering	[126]
$\text{SiGe} + (2, 4, 6, 8, 10 \text{ wt.}\%) \text{ TiB}_2$	Ball milling + hot pressing	[108]

3. Modulation Doping

Modulation doping is a well-recognised concept to increase the conductivity in heterojunction devices [127]. The main idea behind modulation doping is to use the offset in the band structure between two semiconductors in combination with heavy doping of the material with a wider bandgap so that there is a transfer of carriers from the wide bandgap to the narrow bandgap material. The transferred carriers create two-dimensional electron gas, and they are essentially separated from the donor phase, which consequently increases the charge carrier mobility [128]. Conventionally, this strategy was employed to create *p*-channel devices, called modulation-doped field-effect transistors (MODFET) [129]. The difference between energy filtering and modulated doped samples is shown schematically in Figure 5. In the case of modulation doping, the secondary phase increases the conductivity by donating electrons to the host semiconductor, while in the case of energy filtering, the secondary phase scatters electrons and reduces mobility.

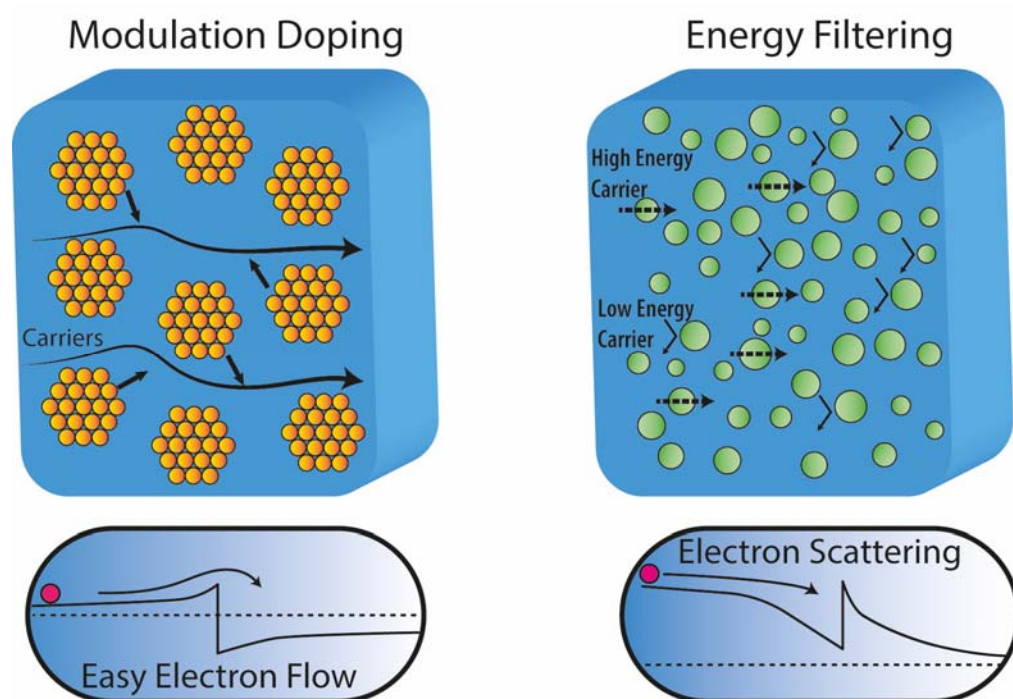


Figure 5. Comparison between a modulated doped semiconductor and a multiphase compound benefiting from energy filtering.

The thermoelectric research community has also used this mechanism to enhance the thermoelectric performance of materials [15,23,25,29,38]. For thermoelectric materials, a combination of two effects has enhanced the thermoelectric efficiency in the modulated doped materials: firstly, a large increase in the electrical conductivity and mobility of the charge carriers [130], and secondly, a reduction in the lattice thermal conductivity as a result of the scattering of phonons by nanostructuring [23,131].

Some attempts have also been made to explore the possibility of using modulation doping in structures similar to field-effect transistors (FETs) [129]. In this adopted structure, the thermoelectric semiconductor nanowire (channel) is enclosed by the heavily doped layer (gate) [132–136]. A modest increase in the power factor was achieved by this approach.

Table 2 summarises the sample compositions, fabrication methods, and corresponding references of recent studies that employed modulation doping to enhance the thermoelectric performance of multiphase materials.

Table 2. Sample compositions and fabrication methods of references that employed modulation doping to enhance the thermoelectric performance of multiphase materials.

Composition	Fabrication Method	Ref.
$\text{Ba}_8(\text{Al}_x\text{Ga}_{1-x})_{16}\text{Ge}_{30}$ ($x = 0, 0.20, 0.23, 0.25, 0.33, 0.50$, and 1)	Casting (each phase separately) + ball milling + sintering	[137]
$\text{AgBiSe}_2 + \text{Bi}_4\text{Se}_3$		[138]
$\text{Cu}_2\text{SnS}_3 + (0, 1, 3, \text{ and } 5\% \text{ mol}) \text{ CuCo}_2\text{S}_4$	Casting (each phase separately) + ball milling + sintering	[25,139]
$\text{Si}_a(\text{Mg}_2\text{Si} + x \text{ at. } \% \text{ Bi})_{1-a}$ ($a = 0.39, 0.50, 0.56, 0.59$, and 0.67 ; $x = 0.3, 0.8, 1.3, 1.8, 2.5$)	Bi-doped Mg_2Si fabricated using induction melting + melt spinning + sintering	[140]
p -type organic conducting polymer PEDOT:PSS + Ge	PEDOT:PSS coated with Ge layer	[141]
$(\text{Ge}_2\text{Te}_2)_x(\text{CuInTe}_2)_{1-x}$ ($x = 98, 95, 90, 87.5, 85, 70, 30$, and 10%)	Casting + hand milling + hot pressing	[142]
$\text{BiCuSeO} + \text{Bi}_{0.8}\text{Pb}_{0.2}\text{Cu}_{0.8}\text{Ni}_{0.2}\text{SeO}$	Each phase was fabricated by Mechanical alloying + ball milling of mixture + sintering	[143]
$\text{BiCuSeO} + \text{Bi}_{0.8}\text{Er}_{0.2}\text{CuSeO}$	Each phase was fabricated by ball milling + sintering. The final composition was obtained by ball milling + sintering	[144]
$\text{BiCuSeO} + \text{Bi}_{0.8}\text{Ba}_{0.2}\text{CuSe}_{0.8}\text{Te}_{0.2}\text{O}$	Each phase was fabricated by mechanical alloying + milling the mixture + sintering	[145]
$\text{Pb}_{(1-x)}\text{Na}_x\text{Te}_{0.65}\text{S}_{0.25}\text{Se}_{0.1}$ ($x = 0.005, 0.01, 0.0015, 0.02, 0.025$, and 0.03)	Casting PbSe and PbS + mixing stoichiometric amounts of PbSe, PbS, Pb, Te, and Na (casting) + sintering	[29]
$\text{Pb}_{0.97}\text{Na}_{0.03}\text{Te}_{(1-x)}\text{S}_x$ ($x = 0.1, 0.15, 0.2, 0.25, 0.3$, and 0.35)	Casting + hand milling + sintering	[146]

4. Phonon Scattering

When it comes to designing a thermoelectric material, the main goal is to maintain a high electrical conductivity while, at the same time, reduce the thermal conductivity to reach an amorphous solid [147]. In semiconductors, phonon transport plays a significant role in thermal conductivity [148,149]. Increasing phonon scattering has, therefore, proven to be a key strategy to improve the efficiency of thermoelectric materials [150]. This is mainly performed by nanostructuring of the material [151], introducing grains with sizes larger than the mean free path of the charge carriers but smaller than the mean free path of the phonons [152], alloy scattering with additional mass or strain fluctuation [153–155], nanocomposites [156–159], and embedding interfaces by creating texture between the two materials [160].

In thermoelectric materials, the phonon-scattering mechanisms are assessed using models for the total thermal conductivity. Traditional models are from Klemens [161], Holland [162], and Callaway [163]. Impurity scattering, boundary scattering, three-phonon normal process, and Umklapp process are considered in these models, and Matthiessen's rule is employed to determine the overall relaxation time.

The Klemens model has been successfully used to evaluate the contribution of each phase on the lattice thermal conductivity [164,165]. In this model, the thermal conductivity for each type of scattering mechanism is evaluated independently, and the overall thermal conductivity is given by [161]:

$$\kappa_{tot}^{-1} = \sum_i \kappa_i^{-1} \quad (8)$$

For phonon-point defects, the relaxation time is given by [161]:

$$\tau_I = \frac{\Gamma V}{4\pi v_s^3} \omega^4 \quad (9)$$

where v_s is the average sound speed on the material, V is the average atomic volume, and Γ is the mass-fluctuation, phonon-scattering parameter [166]:

$$\Gamma = \frac{\langle \Delta M^2 \rangle}{\langle M \rangle^2} \quad (10)$$

where $\langle M \rangle = \frac{\sum_n c_n \sum_i f_{i,n} M_{i,n}}{\sum_n c_n}$, $\langle \Delta M^2 \rangle = \frac{\sum_n c_n \sum_i f_{i,n} (M_{i,n} - \overline{M}_n)^2}{\sum_n c_n}$, $\overline{M}_n = \sum_i f_{i,n} M_{i,n}$, c_n is the stoichiometry of the n -th component and $f_{i,n}$ is the fraction of the i -th element that is presented in the n -th component. Using this formulation, the effect of the material composition can be inferred from the lattice thermal conductivity.

Effective medium approximation, on the other hand, presents a more simplified version of the formula described above. The model incorporates an interface resistance, called Kapitza resistance (R_K), in series with the inter grain resistance [167]. This model is further developed to consider the shapes, orientations, volume fractions, and thermal conductivities of the phases [160]. For instance, the thermal conductivity of a two-phase material with spherical inclusions is expressed by:

$$\kappa^* = \kappa_m \frac{\kappa_p(1 + 2\alpha) + 2\kappa_m + 2f[\kappa_p(1 - \alpha) - \kappa_r]}{\kappa_p(1 + 2\alpha) + 2\kappa_m - f[\kappa_p(1 - \alpha) - \kappa_r]} \quad (11)$$

where κ_m is the thermal conductivity of the matrix, κ_p is the thermal conductivity of the secondary phase, and f is the volume fraction of the secondary phase. The non-dimensional parameter, α , is the ratio of the Kapitza length, L_K , and the second phase radius, a :

$$\alpha = \frac{L_K}{a} = \frac{\kappa_m R_K}{a} \quad (12)$$

An even more simple model than that which has been used to describe the scattering in multiphase materials is impedance mismatch [152]. The specific acoustic impedance of a material is the analogue of the electrical impedance for electrical circuits. In this case, the acoustic impedance measures the opposition of a system when acoustic pressure is applied to it and its calculated as:

$$Z = \rho v \quad (13)$$

where ρ is the volumetric density of the medium and v_s is the speed of the sound in the medium. At the interface of two materials, the reflection (r) and transmission (t) energy coefficients are [168]:

$$r = \left[\frac{Z_2 - Z_1}{Z_2 + Z_1} \right]^2, \quad t = \frac{4Z_1 Z_2}{(Z_1 + Z_2)^2} \quad (14)$$

where Z_1 and Z_2 are the acoustic impedance of the two materials. Figure 6 illustrates phonon transmission and reflection between two dissimilar materials.

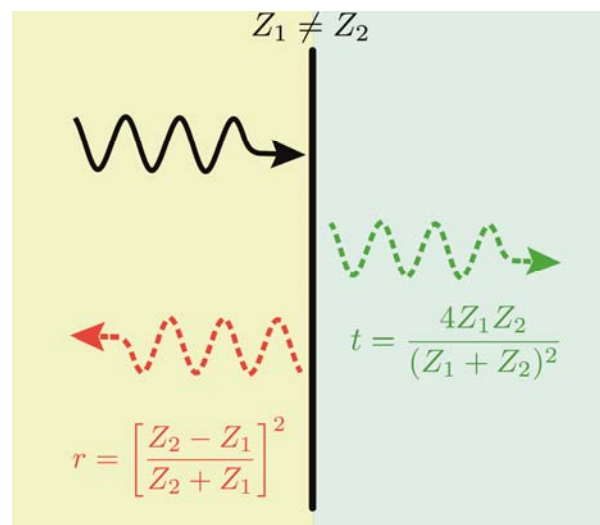


Figure 6. Phonon transmission and reflection due to impedance mismatch.

Experimentally, impedance mismatch between phases has been shown to reduce the thermal conductivity of the bulk material. The impedance mismatch between the PbTe and PbS rich phases in $(\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{1-x}(\text{PbS})_x$ samples led to an inhibition of the heat flow, with the lattice thermal conductivity reaching $0.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the sample with 8% PbS, an 80% reduction in the reported values for the bulk material [169].

In general, phonon scattering has proven to be an effective strategy to reduce the lattice thermal conductivity in multiphase lead telluride-based materials [170–173] and bismuth telluride-based [174–176] materials. For instance, nano-engineered multiphase $\text{PbTe}-x\% \text{ InSb}$ compounds showed an exceptionally low minimum lattice thermal conductivity of $\sim 0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at $\sim 770 \text{ K}$ for 4% InSb and consequently a zT value of ~ 1.83 at 770 K [177]. Even higher zT values of ~ 2 were observed for $\text{Pb}_{(1-x)}\text{Na}_x\text{Te}_{0.65}\text{S}_{0.25}\text{Se}_{0.1}$ compounds [30,31], where the combined effects of phonon scattering at nanoprecipitates and the increase in the power factor due to heterogeneous distribution of dopants between phases were recognised to be responsible for the high TE efficiency. Nano and micro-sized precipitates in $\text{Pb}_{1-x}\text{Ga}_x\text{Te}$ ($x = 0.01, 0.02, 0.03, \text{ and } 0.04$) compounds have shown a reduction in the lattice thermal conductivity, reaching $1.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. A larger fraction of a secondary phase with high thermal conductivity can increase the total thermal conductivity, reported for $\text{PbTe}-\text{Ge}_x$ [178]. Five per cent of GeTe reduced the lattice thermal conductivity to $1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, while a sample with $x = 0.2$ showed a lattice thermal conductivity similar to the pristine sample.

Adding a secondary phase of TiO_2 to a Bi_2Se_3 host increased the Seebeck coefficient by energy filtering and simultaneously reduced the lattice thermal conductivity by 45% [101]. The lattice thermal conductivity of multiphase half-Heusler $(\text{Hf}_{0.6}\text{Zr}_{0.4})\text{NiSn}_{0.99}\text{Sb}_{0.01}$ material was reduced from $\sim 4.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the pristine sample to $\sim 2.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the sample with 20wt.% of tungsten at 300 K [112]; the combined effects of phonon scattering and energy filtering due to the presence of metallic tungsten improved the zT by 55%.

The lattice thermal conductivity values of several single-phase chalcogenides are compared with their multiphase counterparts in Figure 7. The data for single-phase materials were manually extracted from the Materials Research Laboratory Energy Materials Datamining website [179,180]. This dataset contains information of 573 thermoelectric materials from various combinations of host materials and dopants along with several thermoelectric properties measured experimentally at 300 K , 400 K , and 700 K . Here, we have selected the lattice thermal conductivity of chalcogenides, measured at 300 K . Where the lattice thermal conductivity was not available, its value was evaluated using the Wiedemann–Franz law and the Sommerfeld limit for the Lorenz number [181]. Both the bar and boxplot show that the multiphase materials consistently present lower

values of the lattice thermal conductivity. In particular, the boxplot shows that the multiphase materials have, on average, lower values of lattice thermal conductivity.

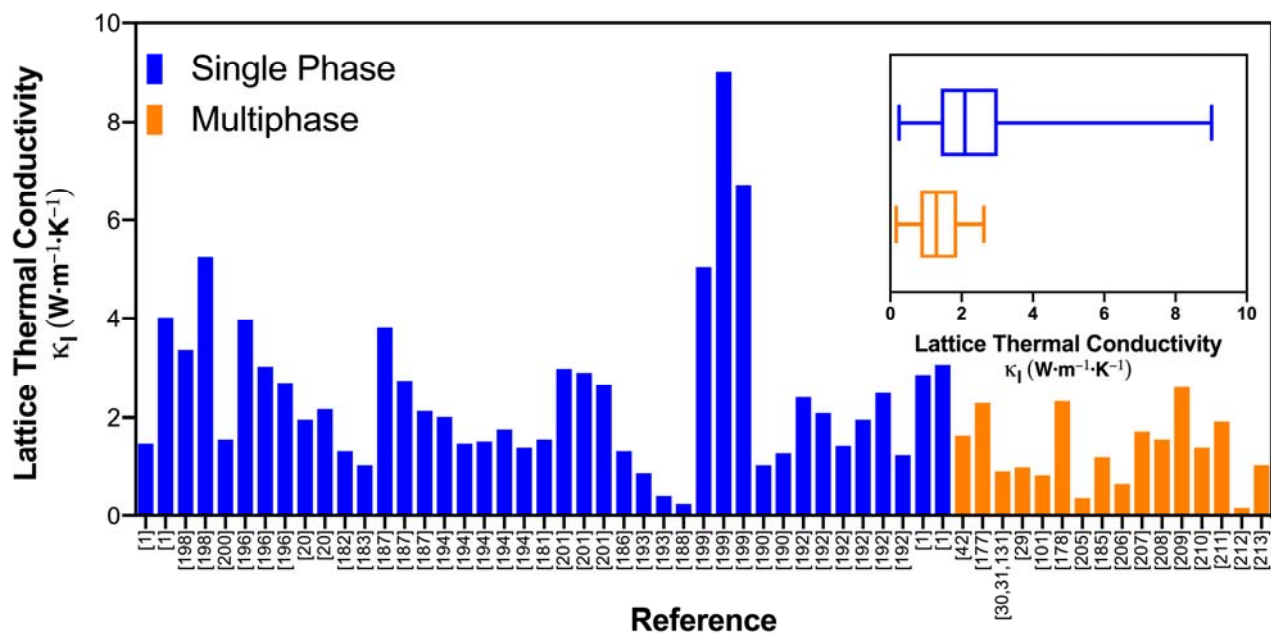


Figure 7. The lattice thermal conductivity of multiphase thermoelectric materials compared with single-phase counterparts; data extracted from [1,20,29–31,42,101,131,177,178,182–213]. The inset shows a boxplot of the same data.

5. Models to Estimate the Transport Properties

In general, multiphase materials can increase phonon scattering, increase the Seebeck coefficient due to energy filtering, and increase electrical conductivity due to modulation doping. These micro and nano effects clearly influence the material on a macroscale. It is, however, of interest to have simplified expressions to predict the behaviour of these materials from the composition and electronic band engineering perspectives. Regarding the thermal conductivity, the effective medium theory allows us to approximate the effective Seebeck coefficient and the electrical conductivity of multiphase materials [214]. There are two main equations to evaluate these properties. The most common equation is the one derived from the usual effective mean theory [215]:

$$\sum_i v_i \frac{\zeta_i - \zeta}{\zeta_i + 2\zeta} = 0 \quad (15)$$

where v_i and ζ_i are the volume fraction and property of phase i , respectively, and ζ is the effective material property. The electrical conductivity can be calculated by setting $\zeta = \sigma$, and the Seebeck coefficient can be calculated by setting $\zeta = S/\sigma$ [216]. The second equation is based on the generalised effective mean theory:

$$\sum_i v_i \frac{\zeta_i^{\frac{1}{t}} - \zeta^{\frac{1}{t}}}{\zeta_i^{\frac{1}{t}} + A \cdot \zeta^{\frac{1}{t}}} = 0 \quad (16)$$

where t is a measure of the grain structure and morphology, and $A = (1 - p_c)/p_c$, where p_c is the percolation threshold. Both parameters can be determined by fitting experimental data, and p_c is estimated from the lattice type and dimensions of the network [217]. The Seebeck coefficient and the conductivity are estimated similar to the previous equation [218].

Recently, models based on electrical networks have been introduced to estimate the electronic properties [214,219,220] and finite element analysis [221]. These latter models

divide the material into pixels (for a 2D analysis) or voxels (for a 3D analysis) grids, where each node corresponds to a fraction of the total volume. Each voxel/pixel is required to be larger than the mean free paths of the carriers and phonons so that the transport is diffusive. Each node is connected to its neighbours by a resistance that is an electric resistance (to calculate the electrical conductivity) and a thermal resistance (to calculate the thermal conductivity) in series with an interface resistance if needed. Following the construction of grids, a nodal analysis will be conducted [222] to determine the temperature and voltage profile of the grids. The Seebeck coefficient is estimated by assigning each node in the electric grid to a local voltage source in series, representing the local Seebeck voltage. By using a Norton equivalent of the voltage source [223], the usual nodal formulation can be applied, and the bulk Seebeck coefficient will be estimated. The general expression is presented as [220]:

$$0 = \sum_{k \neq l} V_{kl} G_{kl} + \sum_{k \neq l} I_{kl} \quad (17)$$

where $V_{k,l}$ is the voltage (or temperature) difference between nodes k and l , $I_{k,l}$ is the current flowing between nodes k and l , and $G_{k,l}$ is the conductivity between nodes k and l . The conductivity will be determined by the local thermoelectric properties of the voxels or pixels:

$$\sigma_{kl}^{-1} = \sigma_k^{-1} + \sigma_l^{-1}, \kappa_{kl}^{-1} = \kappa_k^{-1} + \kappa_l^{-1} \quad (18)$$

where σ_k, σ_l is the electrical conductivity of nodes k and l , respectively, and κ_k, κ_l is the thermal resistivity of nodes k and l .

The main advantage of this approach is that this linear system of equations can easily be solved by electric circuit solvers, and the results can be directly interpreted by engineers. However, the quantum effects are not approximated by an effective medium theory in this model, and therefore, it provides similar accuracy to the more simple models described earlier [219]. Overall, from a design perspective, these equations suggest that the incorporation of highly conductive phases (both thermally and electrically) results in an overall increase in the conductivity of materials. This effect has been experimentally proven in several materials. Graphene, a zero-bandgap material [224], has been successfully used to create thermoelectric materials with high conductivity [225–227], the electrical conductivity of CoSb₃ reached 1.2×10^6 S/m, four times larger than the pristine sample at 300 K [226]. Copper telluride in Bi_{0.5}Sb_{1.5}Te₃ [228] and a composite of ZnSb matrix with minority phases of Zn₄Sb₃, Zn₃P₂, and Cu₅Zn₈ [229] have shown higher electrical conductivity. It should be noted that the values of electronic transport properties are greatly dependent on the fabrication methods [230], quality of the raw materials, and oxidation of the material [231–233].

High-temperature, oxide-based thermoelectric materials have also been shown to benefit from the presence of secondary phases. A multiphase compound of Ca₃Co₄O₉, matrimid polymer + Ag, and carbon black [40] showed a reduction in the electrical conductivity compared to the porous Ca₃Co₄O₉, while the highly conductive phase of Ag reduced a significant deterioration of conductivity.

6. Magnetic Effects

The effects of magnetism on the performance of thermoelectric materials have been investigated for some time, but with less detailed analysis. The idea of spin-wave scattering and magnon drag was proposed in the middle of the last century, where magnon scattering was shown to contribute to an increase in the Seebeck coefficient [234]. Magnons are bosonic quasiparticles, the quanta associated with spin waves [235]. When a magnetic material is subjected to a temperature gradient, the hotter side contains a higher density of magnons that will diffuse towards the cooler side; this magnon flux “drags” the free charge carriers due to the electron–magnon collisions and gives rise to a

second contribution to the Seebeck coefficient, called the magnon thermopower [236]. A hydrodynamical, Galilean based expression for the magnon thermopower is [237]

$$S_{md} = \frac{2}{3} \cdot \frac{C_m}{n_e e} \cdot \frac{1}{1 + \frac{\tau_{em}}{\tau_m}} \quad (19)$$

where C_m is the magnon specific heat capacity per unit volume, τ_m and τ_{em} are, respectively, the transport mean-free time for the electron and magnon–electron collision, e is carrier charge, and n_e is the charge carrier density.

When dealing with magnetism in semiconductors, three main strategies have been proposed to improve the thermoelectric efficiency: (1) optimise thermoelectric properties of magnetic materials using strategies known for non-magnetic materials [43–45,238,239]; (2) introduce a magnetic dopant in a non-magnetic material [46–48,240–243]; (3) introduce a magnetic secondary phase in a non-magnetic material [49,50].

6.1. Magnetic Semiconductors

Examples of magnetic semiconductors are FeSb₂ [244,245], MnTe [246–248], Cr₂Ge₂Te₆ [249], MgAgSb [250], MnSe [251], and FeSe [252]. Experimental results have shown their potential as thermoelectric materials; for instance, a massive Seebeck coefficient of ~27 mV/K has been reported for FeSb₂ (albeit at a low temperature of ~12 K) [253]. It is not easy, however, to establish a causal relationship between magnetism and the Seebeck coefficient. A common method is to check whether a heavily doped sample with a high carrier concentration shows a large value of the Seebeck coefficient [254], because this indicates a possible effect of electron–magnon scattering, which increases the Seebeck coefficient. Fitting mathematical models to the experimental data has also been proposed as a method to identify the magnetic thermopower [255]. Clearly, measuring the transport properties as a function of the magnetic field is the best method to determine the magnetic thermopower [236,256,257].

A spin-dependent Seebeck coefficient can occur in magnetic semiconductors [258]; since the Seebeck coefficients for the two spin channels of spin-up (S^\uparrow) and spin-down (S^\downarrow) are not equal, a spin current proportional to the difference between S^\uparrow and S^\downarrow flows through the magnetic material even in the absence of a charge current [259]. The literature refers to spintronics as the field of study that investigates devices that exploit the properties of electrons spins. In thermoelectricity, this is known as spin caloritronic [260]. This new field of research has attracted the interest of the thermoelectric research community [261–263].

6.2. Magnetic Dopants in Non-Magnetic Semiconductors

Doping non-magnetic thermoelectric materials with magnetic elements has improved the power factor. Magnetic doping of CuGaTe₂ with manganese ions (Mn²⁺) increased the effective mass of the carriers due to the interaction of the magnetic ions and the charge carriers and, consequently, increased the Seebeck coefficient [264]. This effect has also been reported for a Chromium doped Bi₂Te₃ [265]. The negative side effect of magnetic ion dopants is the decrease in the charge carrier mobility that results in a reduction in the electrical conductivity. Overall, the power factor is shown to be increased [266–268].

6.3. Secondary Magnetic Phases

The natural extension of using magnetic elements is to include magnetic phases to enhance the performance of thermoelectric materials [264,269,270]. The magnetic particles of BaFe₁₂O₁₉ in Ba_{0.3}In_{0.3}Co₄Sb₁₂ formed a magnetic composite; BaFe₁₂O₁₉ nanoparticles trap electrons in the ferromagnetic phase due to the spiral motion of the electrons generated by non-uniform spherical magnetic fields. This effectively suppresses the deterioration of thermoelectric efficiency in the intrinsic excitation region [271]. In the paramagnetic phase

(at temperatures above the Curie temperature), though, the nanoparticles release the trapped electrons to increase the carrier concentration in the intrinsic excitation. This effect enhances the overall performance of the thermoelectric material.

Coherent magnetic full-Heusler nanoparticles ($\text{Ti}(\text{Ni}_{4/3}\text{Fe}_{2/3})\text{Sn}$) in a half-Heusler matrix ($\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.5}\text{NiSn}_{0.975}\text{Sb}_{0.025}$) showed significant enhancements of both carrier mobility and the Seebeck coefficient [272]. The magnetic nanoparticles interact with the spin of itinerant carriers, leading to charge localisation (which consequently leads to a decrease in the charge density) and the formation of overlapping bound magnetic polarons (that leads to an increase in mobility).

Interestingly, some magnetic phenomena only occur when the particles are smaller than a certain size [273]. Nanoparticles provide a good platform to take advantage of these magnetic phenomena for the purpose of optimising the thermoelectric performance of materials. If the size of a ferromagnetic nanoparticle is small enough to have only several magnetic domains, it can be magnetised similar to a paramagnet under an external magnetic field, except with a much greater magnetisation. This mechanism is known as superparamagnetism (magnetisation of the nanoparticles can randomly flip direction under the influence of temperature, and they can be magnetised similar to a paramagnet under an external magnetic field [274]). Experimentally, soft magnet transition metals (Fe, Co, or Ni) nanoparticles were embedded in a $\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ matrix [275]. The superparamagnetism fluctuations of the nanoparticles gave rise to multiple scattering of electrons and enhanced phonon scattering. These effects increased the overall thermoelectric efficiency of the material.

In general, secondary magnetic phases introduce a new degree of freedom to enhance thermoelectric materials. The effects of magnetism in semiconductors are not fully understood yet, and general expressions for the contribution of the magnon-drag on the Seebeck coefficient are unavailable yet. The need for more experimental and theoretical investigation presents an opportunity for thermoelectricity.

Table 3 summarises the sample composition and fabrication techniques of recent studies that reported magnetic effects in thermoelectric materials.

Table 3. Sample composition, fabrication technique, and corresponding references which studied magnetic effects in thermoelectric materials.

System	Fabrication Method	Type	Ref.
$\text{CuGa}_{1-x}\text{Mn}_x\text{Te}_2$ ($x = 0, 0.01, 0.02$, and 0.03)	Casting + hand milling + sintering	Magnetic dopant	[264]
$\text{Bi}_{2-x}\text{Cr}_x\text{Te}_3$ ($x = 0, 0.01, 0.02, 0.05$, and 0.10)	Casting + hand milling + sintering	Magnetic dopant	[265]
$\text{Fe}_{3-x}\text{Ti}_x\text{Sn}$ ($x = 0, 0.25, 0.5, 0.75$)	Casting	Magnetic material	[239]
$\text{Sn}_{1.03-x}\text{Mn}_x\text{Te}$ ($x = 0, 0.05, 0.07$, and 0.1)	Casting + cold pelletising	Magnetic dopant	[266]
$\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12} + x \text{ BaFe}_{12}\text{O}_{19}$ ($x = 0.15\%, 0.25\%, 0.35\%$, and 0.45%)	Ball milling + sintering	Magnetic phase	[271]
$\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.5}(\text{Ni}, \text{Fe}_x)\text{Sn}_{0.975}\text{Sb}_{0.025}$ ($x = 0, 0.05, 0.01, 0.15$)	Casting + hand milling + sintering	Magnetic phase	[272]
$\text{Mn}_{1-x}\text{Na}_x\text{Se}$ ($0 \leq x \leq 0.03$)	Ball milling + annealing + hot pressing	Magnetic material	[251]
FeSb_2	Hand milling + annealing + hot pressing	Magnetic material	[244]

Figure 8 compares the maximum zT values reported for several single chalcogenides with their multiphase counterparts. The data for single-phase materials were manually extracted from the Materials Research Laboratory Energy Materials Datamining website [179,180]. Both the bar and violin plot show that the multiphase materials consistently present larger values of zT . In particular, the violin plot shows that many single-phase materials have low zT , while the zT for multiphase materials is distributed towards larger values.

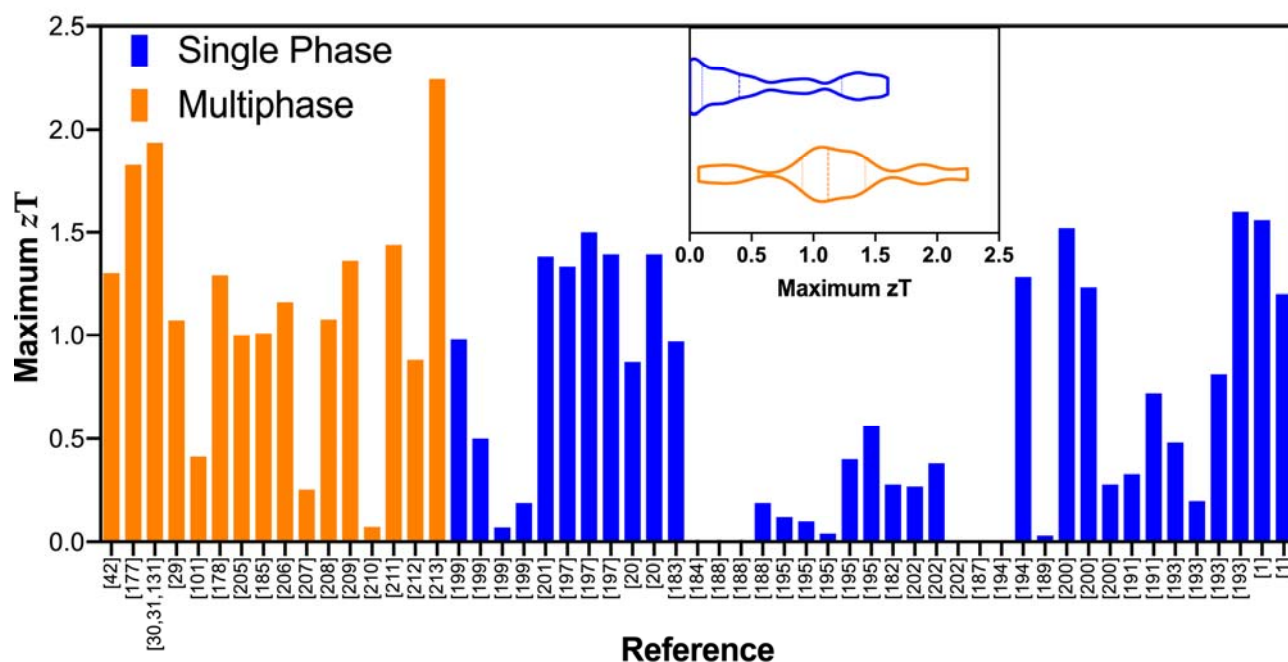


Figure 8. zT values of multiphase thermoelectric materials compared with single-phase counterparts; data extracted from [1,20,29–31,42,101,131,177,178,182–213]. The inset shows the truncated violin plot of the same data, where the dashed line represents the median and dotted lines represent the quartiles.

7. Summary and Outlook

Here, we have reviewed the principal mechanisms and strategies employed to enhance the thermoelectric efficiency of multiphase thermoelectric materials. The interfaces between phases in a material can be utilised to construct potential barriers in the electronic band structure and perform an energy filtering on the charge carriers, where the low energy charge carriers will be filtered/scattered. This can increase the average energy at which the electronic conduction occurs and consequently increase the Seebeck coefficient. The effect of the barrier height can be estimated from the relaxation time approximation from the Boltzmann equation. For a metallic secondary phase, the potential barrier height can be estimated from the work function of the metal and electron affinity of the semiconductor following Schottky's rule. For heterojunctions (two different semiconductors), the potential barrier is proportional to the difference of the electron affinities between the two materials and can be estimated from Anderson's rule. Experimental results have shown that the energy-filtering effect can increase the Seebeck coefficient while decreasing electrical conductivity. The overall result, however, is an increase in the power factor.

Modulation doping is a well-known technique for enhancing the conductivity of semiconductor devices. In this paper, we briefly reviewed the mechanism by which modulation doping is used in multiphase thermoelectric materials.

An increase in phonon scattering due to the presence of secondary phases improves the thermoelectric efficiency of these materials. Secondary phases decrease the relaxation time of the phonons. Traditional models can be employed to verify the effect of a secondary phase on the thermal conductivity of materials. The Klemens model has been used to theoretically explain the reduction in thermal conductivity. The effective medium approximation has been promising in describing the phonon scattering mechanisms of materials with simple structures, such as spherical particles. In an even more simplistic view, for some materials, the transmission and reflection coefficients determined based on the acoustic impedance of the primary and secondary phases can be readily used to evaluate the effect of multiple phases on the reduction of thermal conductivity.

Experimentally, a large increase in the zT has been reported with the use of secondary phases.

Mathematical models based on effective medium theory and networks can also estimate the Seebeck coefficient and electrical conductivity of multiphase materials. These models can be used as a tool to evaluate and tune the properties of thermoelectric materials.

The incorporation of magnetic doping elements and secondary phases in thermoelectric materials has introduced new possibilities to enhance their efficiency. The scattering of electrons due to interactions between charge carriers and magnons can contribute to an increase in the Seebeck coefficient. A magnon flux generated from a temperature gradient “drags” the free carriers and contributes positively to the Seebeck coefficient—this effect is called the magnon thermopower. Experimentally, this has proven to be a promising strategy to enhance the thermoelectric properties of several materials.

Overall, multiphase materials have been shown to be instrumental in achieving high thermoelectric efficiency. Multiple phases allow for more degrees of freedom in the materials design as each phase can be finely tuned to improve selected properties of the multiphase material.

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